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PERCHLORATE ESTER: PREPARATION AND POLYMERIZATION

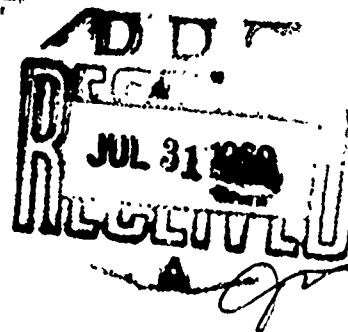
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DIRECTORATE OF MATERIALS & PROCESSES

J. W. CONNOLLY

AERONAUTICAL RESEARCH LABORATORY

SEPTEMBER 1961



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AERONAUTICAL SYSTEMS DIVISION

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PERCHLORATE ESTER: PREPARATION AND POLYMERIZATION

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SEPTEMBER 1961

PROJECT No. 7360

AERONAUTICAL SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

500 - December 1961 - 15-588 & 589

FOREWORD

This report was prepared jointly by the Radiation Studies Section, Radiation Branch, Physics Laboratory and the Chemistry Research Laboratory, Aeronautical Research Laboratories. The work was initiated under Project 7360, "The Chemistry and Physics of Materials", Task 73607, "High Energy Materials Phenomena", and was administered under the direction of the Directorate of Materials and Processes, Aeronautical Systems Division with Dr. Jack Radell and Captain J.W. Connolly acting as project engineers.

This report covers work done during the period 1 January 1960 to 1 January 1961.

ABSTRACT

Epiperchloratohydrin (I) was synthesized and polymerized; although covalent perchlorates are known to be hydrolytically unstable.

Compound (I), dissolved in benzene could be rapidly washed with water without causing major hydrolysis. A simple method for dehydrating silver perchlorate by an azeotropic distillation was used. Compound (I) before and after polymerization was explosive and required special care.

PUBLICATION REVIEW

This report has been reviewed and is approved.

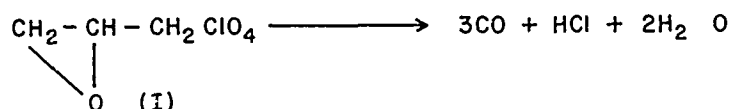
FOR THE COMMANDER:



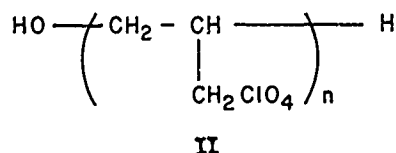
RICHARD J. VOSSLER
Capt, USAF
Chief, Radiation Branch
Physics Laboratory
Directorate of Materials and Processes

INTRODUCTION

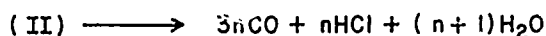
The synthesis of epiperchloratohydrin (I) presented an interesting challenge. It contains the necessary elements to be an internal monopropellant. A material balance for its self-decomposition could be presented as follows:



Compound (I) can be polymerized to polymer, (II). The decomposition of

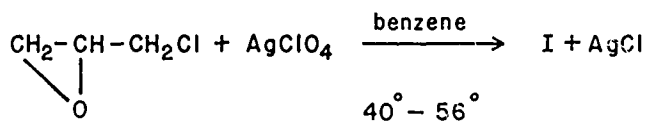


such a polymer may occur thus:



No previously reported covalent perchlorate polymer was found in the literature.

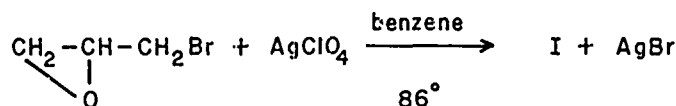
The reaction originally chosen to give product (I) was:



When this reaction was investigated, a method was developed for azeotropically removing water from the silver perchlorate.

The silver chloride precipitated from the reaction in a finely divided form made it difficult to filter. The reaction mixture had to be centrifuged and the solution decanted. With continued heating of the solution, more silver chloride formed, and was removed in the same manner. The formation and removal of silver chloride was repeated 8 times with less silver chloride appearing in each successive step and never entirely removed. When epibromohydrin was used in place of epichlorohydrin, the reaction proceeded

rapidly and the silver bromide formed could be more easily centrifuged than the silver chloride. The method of choice for preparing (I) was:



No attempt was made to study the reaction with epichlorohydrin and silver perchlorate in benzene at 86°.

EXPERIMENTAL

Synthesis and polymerization of epiperchloratohydrin (I). -- Into a 500 ml. r. b. flask fitted with a Dean and Stark distilling trap and a reflux condenser protected by a calcium chloride filled drying tube was added 48.5 grams of "anhydrous" silver perchlorate and 250 ml. of ACS benzene. The solution was refluxed for 30 minutes and 3.5 ml. of water collected in the trap leaving 45 g. of AgClO_4 (.22 mole). The solution in the flask changed from colorless to a clear light amber. A teflon covered egg-shaped magnetic stirring bar was placed in the flask. The Dean and Stark distilling trap was replaced by a baro-static addition funnel. Over a period of 30 minutes, 26.7 g. (.20 mole) of (III) was added dropwise to the stirred and refluxed solution. The reaction occurred immediately. Heating and stirring of the water bath was discontinued 5 minutes after the addition was completed. The solution was decanted from the silver bromide. The washed and dried silver bromide weighed 23.7 g. (.13 mole, 64.9 percent). The solution was diluted with 150 ml. of benzene and washed with distilled water (6-200 ml. portions) until the washes did not precipitate when treated with a few drops of concentrated hydrochloric acid. The benzene solution remaining in the separatory funnel was treated with granular anhydrous sodium sulfate, filtered through glass wool and concentrated at 56° and 150 mm. while being stirred vigorously with the teflon covered magnetic bar. There remained 16.6 g. (.11 mole and 54.7 percent) of (I). An ethylene chloride-dry ice trap was used during solvent removal to protect the pump. Attempts to distill (I) at 12 mm. and 56° caused the residue to darken and the distillation was stopped.

Anal. Calcd for (I): saponification equivalent, 156.5. Found: saponification equivalent, 148.

After standing at room temperature for 24 hours, (I), which was very fluid, darkened and polymerized to a viscous, sirupy mass. The resulting polymer (II), unlike (I), was not soluble in benzene.

Anal. Found for (II): saponification equivalent, 180. The rate of polymerization was qualitatively observed to be much slower at 6°.

The reaction of epilodohydrin and silver perchlorate was considerably more vigorous than with the corresponding chloro and bromo-compounds. As a result this reaction was not explored further.

DISCUSSION

Although it would have been desirable to distill (I), this was not feasible because of its sensitivity. However, the analysis and method of preparation agree with the proposed structure. An inventory of the reaction mixture indicate the possible presence of the following: (I), (III), silver perchlorate, silver chloride, and benzene. The silver bromide precipitated quantitatively in the presence of the water wash. The silver perchlorate is very soluble in water and easily removed by the water wash from the benzene solution. Furthermore, a test of the wash water showed the silver perchlorate had been quantitatively removed. The solubility of epibromohydrin at 25° was found to be 2 g. in 100 g. of water and very soluble in benzene. The solubility of (I) is much greater in benzene than in water. Any HClO_4 which might have formed would be insoluble in benzene and would be readily soluble and removed by the water washes. The only products which might have remained are (I) and (III). The analysis indicates the overwhelming presence of (I). On mere contact of (I) with water a milky solution resulted while the epichlorohydrin remained clear and immiscible even after shaking. From the time of formation of (I), as indicated by the AgBr , to its isolation after washing there was a drop of about 10 percent in yield of the product. Compound (I), when treated with aqueous sodium hydroxide in determining saponification equivalent, did not dissolve until refluxed with periodic shaking for one hour.

During the preliminary screening, solvents other than benzene investigated for reacting silver perchlorate and epibromohydrin were: dioxane, acetone, ethanol, dimethyl formamide, cyclohexane, tetrahydrofuran, and methyl chloride. The reaction proceeded most completely and rapidly in benzene.

A further screening effort was made to determine the reactivity of silver perchlorate with some aromatic halogen compounds. The results were tabulated:

<u>compound</u>	<u>solvent</u>	<u>result</u>
2, 4-dinitrochlorobenzene	benzene	no reaction
2, 4-dinitrochlorobenzene	tetrahydrofuran	no reaction
1-bromo-3-chlorobenzene	benzene	no reaction
1-bromo-2-iodobenzene	benzene	no reaction
1-bromo-4-nitrobenzene	benzene	no reaction
1-bromo-2-nitrobenzene	benzene	no reaction
p-nitrobenzyl chloride	benzene	precipitate

CAUTION

All attempts to ignite either (I) or (II) resulted in violent explosions. Both (I) and (II) are shock sensitive. No explosions were ever encountered during the synthesis or washing of (I). When the last traces of benzene are removed from (I), under vacuum, explosions have occurred at temperatures as low as 25°. Explosions have also occurred

in the dry-ice cooled trap after solvent was removed from (i) and the vacuum was released. Compound (I) exploded at room temperature while at rest under a layer of n-dodecane. Both (I) and (II) could be rendered harmless by treatment with aqueous sodium hydroxide and heat (saponification). Compounds (I) and (II) were discarded by treatment with aqueous sodium hydroxide and flushing down the drain with copious quantities of water.